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RESEARCH ARTICLE

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Selective recognition of Cr (VI) ion as $Cr_2O_7^{2-}$ in aqueous medium using CTAB-capped anthracene-based nanosensor: Application to real water sample analysis

Sonali B. Suryawanshi^{1,2} | Prasad G. Mahajan³ | Govind B. Kolekar¹ | Anita J. Bodake² | Shivajirao R. Patil¹

¹Fluorescence Spectroscopy Laboratory, Department of Chemistry, Shivaji University, Kolhapur, India

²Department of Chemistry, Rajaram College, Kolhapur, India

³Department of Chemistry, Kongju National University, Gongju, Republic of Korea

Correspondence

Anita J. Bodake, Department of Chemistry, Rajaram College, Kolhapur 416004, India. Email: anitabodake07@gmail.com Shivajirao R. Patil, Fluorescence

Spectroscopy Laboratory, Department of Chemistry, Shivaji University, Kolhapur 416004, India. Email: srp_fsl@rediffmail.com

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Department of Science and Technology, Government of India, New Delhi, India; University Grants Commission (UGC), Government of India, New Delhi, India

Abstract

Surfactant-capped nanoparticles of 9, 10-diphenyl anthracene prepared by reprecipitation method found highly fluorescent due to aggregation-induced enhanced emission (AIEE). Cetyltrimethyl ammonium bromide (CTAB) surfactant not only generated positive zeta potential on the surface of nanoparticles to attract anions of interest but also stabilized nanoparticles into brickshape morphology. The fluorescence of nanoparticles is quenched by $Cr_2O_7^{-2}$ ion very significantly in comparison with other diverse ions, namely, MnO₄, $S_2O_8^{2-}$, HCO₃, and Cr₂O₄²⁻. Though S²⁻ and IO₃⁻ showed increase in the fluorescence of nanoparticles, the interference found is negligible in the Cr (VI) analysis. The selectivity and sensitivity of nanoparticles for recognition of $Cr_2O_7^{2-}$ were explored by systematic fluorescence titration. The fluorescence quenching data fits into the usual Stern-Volmer equation. A calibration curve constructed by plotting quenching of fluorescence (ΔF) against concentration of Cr (VI) exhibiting a linear fit in the equation, $\Delta F = 3070x$, is used for the estimation of chromium concentration (x). The correlation coefficient value $R^2 = 0.998$ obtained from curve is nearly equal to 1 indicates linear fit between quenching data and concentration of Cr (VI). The estimated values of limit of detection (LOD) in the method 0.01392 μ g.mL⁻¹ is far below the permissible value of Cr (VI) 0.05 µg.mL⁻¹ in drinking water approved by world health organization (WHO) and United State Environmental Protection Agency (USEPA). The proposed method of Cr (VI) detection is applied for real sample collected from hard chrome deposition industry from nearby region. The amount of Cr (VI) estimated by present method is comparable with AAS determination for the same samples.

KEYWORDS

aggregation induced enhanced emission, Cr (VI) ion, CTAB, Diphenylanthracene nanoparticles, electrostatic interaction

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1 | INTRODUCTION

Among the elements, chromium is obviously of particular interest as it is widely distributed in the environment because of its many industrial applications like galvanization, steel industry, lather tanning, chrome plating, etc.^{[1-} ^{4]} Chromium decorative finishes are applied on a number of decorative articles like cycle components, automobile components, household articles, and office furnitures.^[5] In industry, thick chromium is used as hard chrome and used to coat components to obtain resistance to wear and tear so as to improve service life of the components.^[6] In aqueous system, the dominate species of chromium are Cr (VI) and Cr (III) that are present in waste water drained from such industries. Of these two, Cr (VI) is highly toxic and carcinogenic and reported to be the second most inorganic contaminates in ground water at hazardous waste site.^[1] In the United States, the Environmental Protection Agency (EPA) list it as a hazardous air pollutant under clean water act and hazardous constituents under the Resource Conservation and Recovery Act.^[7] According to world health organization (WHO) and United State Environmental Protection Agency (USEPA), the permissible level of Cr (VI) in drinking water is 50 μ g L⁻¹ (ie, $0.05 \ \mu g \ mL^{-1}$).^[7] Whereas the Agency for Toxic Substances and Diseases Registry (ATSDR) and Minimal National Standard (MINAS) classify Cr (VI) as the top 18th hazardous substance and upper limit in industrial waste water is 100 μ g L⁻¹ (0.1 μ g mL⁻¹).^[8] Because of low-cathodic efficiency and high-solution viscosity, a toxic mist of water and hexavalent chromium is released from the bath.^[9] Even though discharge from wet scrubber treated to precipitate the chromium from solution, it is not guaranteed that it cannot remain in the waste water. Accurate determination of each species of chromium rather than total concentration level is required to evaluate physiological and toxical effects. Cr (VI) is relatively more mobile than Cr (III), therefore, readily penetrates cell membrane where it is reduced to Cr (III) and subsequently binds to macromolecules.^[10,11] Consequently, there is a need to develop simple, accurate, and reliable method for sensing and detection of Cr (VI) and to create legal norms by overcoming interference of Cr (III).^[12] 1,5-diphenyl carbazide¹⁰, atomic absorption spectroscopy,^[13] inductively coupled plasma atomic emission spectroscopy (ICP-AES),^[14,15] and electrochemical^[16] are the techniques used currently for quantification of Cr (VI). Of these, electrochemical method is simple but suffers from the interference of Cr (III). For the analytical laboratories with cost concern with such system do not have to be high-end system. Since, only isocratic elution is needed for separation of chromium species. In addition, both atomic absorption spectroscopy (AAS) and inductively coupled plasma (ICP) are time-consuming and require

tedious procedure of sample preparation.^[17] On the contrary, the fluorimetric methods based on use of suitable probe sensitive to Cr (VI) would be a simple and costeffective for analysis.^[18,19] Cr (VI) in aqueous system is measured as $Cr_2O_7^2$ ion, and hence, search of surface modified fluorescent organic nanoparticles to attract divalent chromate would give new sensory system. The surface of nanoparticles of fluorescent diphenylanthracene prepared in the laboratory was charged by using cetyltrimethyl ammonium bromide (CTAB) surfactant so as to generate positive zeta potential in the reprecipitation method.^[20,21] The surfactant-capped Fluorescent Organic Nanoparticles (FONs) could electrostatically attract oppositely charged ionic species because of desired charge generated over the surface of nanoparticles (NPs). Anthracene derivatives are widely used probes in micellar solution and nonaqueous medium.^[22] Choice of diphenyl anthracene (DPA) is because of its hydrophobicity required for preparation of nanoparticles and high-quantum efficiency of fluorescence.^[23] The addition of dichromate ion in the vicinity of DPANPs found to quench significant fluorescence while other anions respond very negligibly. Thus, an attempt has been performed to establish a new procedure for the selective recognition of Cr (VI) ion in aqueous suspension by fluorescence quenching approach.

2 | EXPERIMENTAL

Analytical grade ethanol procured from Changshu Yangyuan Chemical, China and acetone purchased from S. D. Fine Chemicals were used with further purification. 9,10-Dibromoanthracene, 1,1-Bis (diphenylphosphino)ferrocene) dichloropalladium (II) [Pd (dppf)Cl₂], and salts of all metal cations were procured from Sigma Aldrich (India). Ultrapure water was used for the preparation of solutions in all experiments. Cetyltrimethyl ammonium bromide was obtained from Loba chemie Mumbai (India).

2.1 | Characterization techniques

Nuclear magnetic resonance (NMR) spectra were recorded in deuterated chloroform (CDCl₃) on Bruker AC-300 NMR spectrometer (300 MHz for ¹H NMR and 75 MHz for ¹³C NMR). Chemical shifts are reported using tetramethylsilane (TMS) as an internal standard. The particle size distribution and zeta potential of nanoparticles in aqueous suspension were measured using a Malvern Zetasizer (Nano ZS-90) equipped with 4 MW, 633 nm, He-Ne Laser (the United Kingdom) at 25°C under fixed angle of 90° in disposable polystyrene cuvettes. A Field Emission-Scanning Electron Microscope (FE-SEM, FEI Quanta 650 F) was used to examine the morphology of surfactant-capped NPs. UV-vis absorption spectra were recorded by (Specord 210 plus) the Analytical Jena using 1 cm quartz cell. Steady-state fluorescence spectra of solutions were recorded on Spectrofluorimeter (JASCO, Model FP-8300, Japan). The excitation and emission slits were fixed at 5 nm. The fluorescence lifetime was measured at $\lambda_{ex}/\lambda_{em} = 291$ nm/452 nm using a Time-Correlated Single Photon Counting (TCSPC) Spectrometer HORIBA Jobin Yvon IBH, Japan.

2.2 | Synthesis of 9, 10-DPA

9, 10-dibromoanthracene (1.0 mmol), phenyl boronic acid (1.2 mmol), NaOH (0.8 g, 2 mmol), and 1, 1-Bis (diphenylphosphino ferrocene) dichloropalladium (II) (Pd (dppf) Cl₂) (0.0085 g, 1 mol %) were taken in round bottom flask, dissolved in ethanol (5 mL). The reaction mixture was stirred in an oil bath at 80°C. The progress of reaction was monitored by TLC using n-hexane: ethyl acetate (9:1) as solvent system. After completion of reaction, the content was poured into water (10 mL). The filtrate was extracted with diethyl ether. The organic layer was collected, dried over anhydrous Na₂SO₄ and concentrated under vacuum to afford the product.^[23,24] Scheme 1 shows synthesis route of DPA. DPA was obtained as slight yellow powder, 80 % yield, melting point 246°C (literature 245-248°C), ¹H NMR (300 MHz, $CDCl_3$): (Figure S1) δ7.42 to 7.34 (m, 3H), 7.55 to 7.50 (m, 4H), 7.69 to 7.58 (m, 7H), and 7.74 to 7.71 (m, 4H) ppm. ¹³C NMR (75 MHz, CDCl₃): (Figure S2) δ 125.0, 126.9, 127.4, 128.4, 129.8, 131.3, 137.1, 139.1 ppm.

2.3 | Preparation of CTAB-capped 9, 10-DPANPs

The CTAB-capped nanoparticles of 9, 10-Diphenylanthracene were prepared by reprecipitation method developed in the laboratory.^[25] The stock solution of DPA (1×10^{-5} M) in acetone was prepared and stored in dark place. Two milliliters of this acetone solution was rapidly injected through microsyringe into 100 mL aqueous solution of CTAB (2×10^4 M) at room temperature with vigorous stirring for 1 hour and further sonicated for 30 minutes in sonicator (Model UCB 40,



SCHEME 1 Synthesis of 9, 10-diphenyl anthracene

India) to attain the uniform dispersion of nanoparticles in aqueous suspension. The role of CTAB is not only to stabilize the NPs but also to generate a positive surface charge over the surface of NPs.

3 | **RESULTS AND DISCUSSION**

3.1 | Particle size and morphology studies of CTAB-capped DPANPs

Formation of NPs as aqueous suspension were examined by particle-size analysis based on DLS. Figure 1 shows the particle size distribution histogram of DPANPs recorded using dynamic light scattering (DLS) technique. The average particle size obtained from DLS analysis is 72 nm while the zeta potential value given by zeta sizer analysis is 39 mV indicates good stability of NPs. The zeta potential in the range from 30 to 60 mV indicates good stability of nanoparticles in aqueous suspension.^[26] FE-SEM image of air-dried film of aqueous suspension of NPs prepared on silicon substrate is shown in Figure 2. The FE-SEM image shows a brick-shaped uniformly distributed particles, and the average particle size is 166 nm. The particle size of NPs obtained from FE-SEM analysis is relatively large as compared with the value obtained from DLS technique because of agglomeration of nanoparticles when water evaporated from aqueous suspension of NPs placed on the substrate.

3.2 | Photophysical studies of CTAB-capped DPANPs

3.2.1 | Absorption and fluorescence properties of CTAB-capped DPANPs

The absorption spectrum of aqueous suspension of CTAB-capped DPANPs (A) and absorption spectrum of dilute solution of DPA in acetone (B) is shown in Figure 3. The absorption spectrum of CTAB-capped DPANPs shows intense broadband with maximum at 270 nm whereas the absorption spectrum of DPA in acetone is structured peaking at 358, 376, and 396 nm. The absorption spectrum of CTAB-capped DPANPs suspension is blue shifted compared with absorption spectrum of dilute solution of DPA molecule in acetone. The spectral shift indicates formation of H-type aggregates (ie, face-to-face interaction) because of lateral π -stacking effect between molecules.^[27] The fluorescence spectrum (A) of DPANPs shown in Figure 4 is an intense band with maximum at 452 nm and is red shifted from the fluorescence spectrum of DPA in acetone solution (spectrum D) because of aggregation. The nonradiative path in



FIGURE 1 Particle size distribution histogram of cetyltrimethyl ammonium bromide-capped DPANPs obtained by DLS analysis



FIGURE 2 Field emission-scanning electron microscope image of air dried film of cetyltrimethyl ammonium bromide-capped DPANPs (brick-shape morphology)

aggregated cluster is blocked by restricted intramolecular rotation, which, in turn, opens up a radiated channel resulting into intense fluorescence from NPs commonly known as AIEE.^[28,29] However, weak intensity of emission of DPA monomer in acetone is due to dissipation of energy in molecular rotation and vibrations.^[30] The excitation spectrum of NPs (B) shown in Figure 4 reveals maximum at 291 nm and shifted towards shorter wavelength in comparison with the excitation spectrum of DPA in acetone (spectrum C) appeared with maximum at 370 nm. The Stokes shift estimated as a difference between excitation and emission maxima for nanoparticles ($\Delta \bar{\nu} = 15285.00 \text{ cm}^{-1}$) is higher than that estimated

for monomer molecule in acetone ($\Delta \bar{v} = 2850 \text{ cm}^{-1}$). The larger Stokes shift is an indication of strong intermolecular forces between molecules in nanoaggregates.

3.2.2 | Fluorescence lifetime of CTAB-capped DPANPs

The decay profile of dilute solution of DPA in acetone (B) and of aqueous suspension of CTAB-capped DPANPs (A) are shown in Figure 5. The fluorescence lifetime 10 ns of NPs is relatively longer than that of DPA in acetone (5.2 ns). The aggregated molecules stay in the excited



FIGURE 3 Absorption spectra of diphenyl anthracene in acetone (spectrum B) and cetyltrimethyl ammonium bromide-capped DPANPs suspension (spectrum A)



FIGURE 4 Fluorescence emission A, and excitation B, spectra of aqueous suspension of cetyltrimethyl ammonium bromide-capped DPANPs, excitation C, and fluorescence emission D, spectra of diphenyl anthracene in acetone



FIGURE 5 Fluorescence decay profiles of aqueous suspension of cetyltrimethyl ammonium bromide-capped DPANPs A, and dilute solution of diphenyl anthracene in acetone B,

state for longer time, and therefore, restricted molecular rotation and vibration of molecules in nanoaggregate increase fluorescence lifetime of NPs.^[21]

3.3 | Stability experiment of fluorescence intensity of CTAB-capped DPANPs

The study of effect of pH on NPs is a vital parameter owing to its impact on spectral property. The effect of pH on fluorescence intensity of CTAB-capped DPANPs in aqueous suspension by using Phosphate buffer was studied, and results are given as supporting information (Figure S3). The NPs are stabilized by cationic surfactant CTAB, and therefore, the intensity of NPs expected to depend upon pH of the solution. It is seen that the fluorescence intensity of the aqueous suspension of NPs is maximum at pH 5. Hence, the pH 5.0 was maintained in further experiments. Feasibility of prepared fluorescent nanoparticles is of importance in practical applications particularly pertaining to the pH effect and photostability.^[31] It is found that the emission intensity of aqueous suspension of as prepared NPs is 7428.67 arbitrary unit (au), which after a week, found nearly same 7209.67 au. This observation indicates excellent photostability of NPs for more than a week.

3.4 | Fluorescence based recognition test of CTAB-capped DPANPs for anions

The change in fluorescence intensity of aqueous suspension of CTAB-capped NPs was measured in presence of solutions containing anions, namely, MnO₄⁻, S²⁻, $S_2O_8^{2-}$, HCO₃⁻, IO₃⁻, NO₃⁻, Cr₂O₇²⁻, and other forms of Cr like Cr₂O₄²⁻ ie, Cr (III) of concentration $1.2 \,\mu g \, m L^{-1}$ each. Figure 6A shows the fluorescence spectra of CTAB-capped DPANPs without and with solution of anions. From Figure 6A, it is seen that the fluorescence intensity of NPs at $\lambda_{em} = 452$ nm reduced significantly by $Cr_2O_7^{2-}$ ion, whereas other anions responded very negligibly except IO₃⁻, S²⁻, which actually increases the fluorescence intensity of NPs negligibly. IO₃⁻ and S²⁻ though increasing the fluorescence of sensor when added independently but their addition as interfering ion with Cr (VI) actually did not change the quenching data much as revealed in the bar diagram presented in Figure 6B. The height of bar (blue) of extent quenching induced by Cr (VI) alone is similar to bar (red) presenting quenching by Cr (VI) in the presence of interfering IO_3^- and S^{2-} . The interference of divers ions is also considered for selective sensing of NPs towards $Cr_2O_7^{2-}$ ion. The result of change in fluorescence intensity of NPs by different anions in the presence of $Cr_2O_7^{2-}$ ion is represented by





FIGURE 6 A, Fluorescence spectra of aqueous suspension of cetyltrimethyl ammonium bromide-capped DPANPs in presence of various anion solutions monitored at excitation wavelength 291 nm. B, Bar diagram of fluorescence intensity change [$\Delta F/F$] of the cetyltrimethyl ammonium bromide-capped DPANPs solution in the presence and absence of Cr₂O₇²⁻ and coexisting anions (1.2 µg mL⁻¹ excitation wavelength 291 nm)

bar diagram in Figure 6B. The lowering seen in the height of first blue bar representing the different anions other than $Cr_2O_7^{2-}$ are considerably short as compared with the height of first blue bar presenting $Cr_2O_7^{2-}$. Similarly, height of the red bar presenting the effect of interfering ion on the quenching of fluorescence of NPs with $Cr_2O_7^{2-}$ is comparable with the height of first red bar presenting quenching of NPs. The effect of concentration of $Cr_2O_7^{2-}$ was studied by adding gradually increasing amounts of its solution in the range from 0.0 to $1.2 \ \mu g \ m L^{-1}$ in known volume of aqueous suspension of NPs maintained at pH 5.0. The fluorescence spectra of solution of NPs presented in Figure 7 reveal that the



FIGURE 7 Fluorescence spectra of cetyltrimethyl ammonium bromide-capped DPANPs suspension in the presence of different amounts of $Cr_2O_7^{2-}$ anion (0.0, 0.05, 0.2, 0.3, 0.35, 0.4, 0.5, 0.6, 0.7, 0.8, 1.2 µg mL⁻¹) in phosphate-buffered (pH = 5) solution at excitation wavelength $\lambda_{ex} = 291$ nm

intensity of fluorescence at 452 nm decreases gradually with increasing in concentration of solution of $\text{Cr}_2\text{O}_7^{2-}$ ions without any spectral modification. The fluorescence quenching data are analyzed by using the usual Stern-Volmer equation given below.

The plot of $\frac{F_0}{F}$ Vs concentration of Cr₂O₇²⁻ ion solution given in Figure 8 with error bar is straight line with intercept 1 validates the Stern-Volmer equation.

$$\frac{F_0}{F} = 1 + K_{SV}[Q] = 1 + k_q \tau_0[Q], \qquad (1)$$

where F_0 and F are the fluorescence intensities of NPs in absence and in presence of $Cr_2O_7{}^{2-}$ solution of different



FIGURE 8 Stern-Volmer plot of F_0/F or τ_0/τ versus addition of different amounts of $Cr_2O_7^{-2-}$ solution with error bar (0.0, 0.05, 0.2, 0.3, 0.35, 0.4, 0.5, 0.6, 0.7, 0.8, 1.2 µg mL⁻¹)

concentration, K_{sv} is the Stern-Volmer quenching constant estimated from the slope of the graph, and the value is $6.030 \times 10^4 \text{ M}^{-1}$. Q is the concentration of the $\text{Cr}_2\text{O}_7^{2-}$ ion solution while k_q is the quenching rate constant. τ_0 is the fluorescence lifetime of NPs without $\text{Cr}_2\text{O}_7^{2-}$ whose value obtained from Figure 5 is taken for calculation of quenching rate constant (k_q). The calculated value of k_q is $6.030 \times 10^{12} \text{ M}^{-1}$ second⁻¹. The fluorescence quenching data fits into the following geometrical Equation 2.

$$y = 0.603x + 1$$
 (2)

The linear relationship between ratio of fluorescence of probe without and with $Cr_2O_7^{2-}$ ion, ie, response of analyte signal and concentration of analyte solution examined from the computational value of correlation coefficient (R^2). The value of R^2 0.998, which is very close to 1 indicates linear relationship between two variable arising in S-V equation. In order to explore suitability of Stern-Volmer plot for quantification of Cr (VI) ion solution from real sample, the lower detection limit is calculated as limit of detection (LOD) using the following equation.

$$LOD = \frac{3.3\sigma}{K_{sv}},$$
 (3)

where σ' is the standard deviation of y intercept of the regression line, and "K_{sv}" is the slope of the calibration graph. The LOD of the method is 0.01392 µg mL⁻¹.

3.5 | Mechanism of quenching of fluorescence of NPs by $Cr_2O_7^{2-}$

The negatively charged dichromate ion is believed to attract electrostatically towards the opposite charge generated by CTAB on the surface of NPs and gets adsorbed. The possible interaction between polar part of CTAB and $Cr_2O_7^{2-}$ ion destabilizes the nanoparticle by which intensity of fluorescence decreases. The fluorescence appearing in presence of $Cr_2O_7^{2-}$ ion is because of uninteracted NPs, and therefore, the extent of quenching of fluorescence increases with increase in concentration of $Cr_2O_7^{2-}$ ion in solution. The fluorescence lifetime is a characteristic property and independent of concentration of fluorophor.^[32] The data on lifetime measurement of aqueous suspension of NPs performed in presence of $\operatorname{Cr_2O_7}^{2-}$ ion, presented as $\frac{\tau_0}{\tau}$ versus concentration of $\operatorname{Cr_2O_7}^{2-}$ ion in Figure 8 with, are a straight line parallel to concentration axis. This observation clarifies that lifetime is independent of Cr₂O₇²⁻ amount and indicates static type interaction between them in ground state.

The quenching of fluorescence is because of the adsorption of the Cr (VI), and hence, the concurrency between quenching constant and adsorption constant calculated using Langmuir adsorption isotherm modified for fluorescence given below (Equation 4) would be in support of the proposed mechanism.^[33,34]

$$\frac{C}{F} = \frac{1}{KF_0} + \frac{1}{F}C,$$
(4)

where C is the concentration of $Cr_2O_7^{2-}$ ion, F_0 and F are the fluorescence intensity of nanoparticles without and with $Cr_2O_7^{2-}$ ion. The adsorption equilibrium constant K is the Langmuir binding constant. The binding of $Cr_2O_7^{2-}$ ion on the surface of the nanoparticles can be



FIGURE 9 Plot of C/F as a function of concentration (C) of $Cr_2O_7^{2-}$ anion with error bar (Langmuir adsorption plot)



FIGURE 10 Representation of the average particle size and zeta potential of cetyltrimethyl ammonium bromide-capped DPANPs varies in response to the addition of aqueous solutions of $Cr_2O_7^{2-}$ ^{-0.5} and 1.2 µg mL⁻¹ in cetyltrimethyl ammonium bromide-capped DPANPs (pH = 5)



SCHEME 2 Proposed scheme of formation of cetyltrimethyl ammonium bromide-capped DPANPs and its complexation with $Cr_{3}O_{7}^{2}$ ion

studied by the linearized plot of C/F versus concentration (C) of the $Cr_2O_7^{2-}$ ion solution shown in Figure 9 with error bar. The value of coefficient of linear fit given by plot is 0.994, and the Langmuir binding constant K obtained from slope and intercept is $1.17647 \times 10^4 \text{ M}^{-1}$. The Langmuir adsorption constant is in agreement with the Stern-Volmer quenching constant [Ksv = 6.030 \times 10⁴ M⁻¹]. This observation supports the proposed mechanism of adsorption of $Cr_2O_7^{2-}$ ions on the positively charged surface of nanoparticles. In addition to this, the decrease in zeta potential from 39 to 19.5 mV with increase in concentration of $Cr_2O_7^{2-}$ ion from 0.5 μ g mL⁻¹ to 1.2 μ g mL⁻¹ seen in the bar diagram in Figure 10 led us to consider the destabilization of nanoparticles ultimately resulting in quenching of fluorescence of NPs. Similarly, the particle size, which is seen increased from 72 to 550.0 nm is also an additional support for proposed adsorption of $Cr_2O_7^{2-}$ ion over the surface of NPs. Further, the possible mechanism of electrostatic interaction and surface adsorption of $Cr_2O_7^{2-}$ ion on positively charged surface of DPANPs is revealed in Scheme 2.

3.6 | Application of the surface modified probe for determination of Cr (VI) in environmental water sample and real-water sample from industrial waste

The proposed nanosensor probe system was successfully applied for the quantification of Cr (VI) from environmental and real-water sample using standard addition method.^[35] The river water sample was collected from Panchganga River Kolhapur, (Maharashtra, India). Further, the collected water samples were filtered through Whatmann filter paper no 41 to remove solid impurity and used for further analysis. The water samples were spiked with Cr (VI) to prepare two synthetic samples of concentration 0.24 and 0.58 μ g mL⁻¹ and diluted by water sample so that fluorescence of nanoparticles must be in measuring range of fluorimeter (Table 1). Whereas for real-sample analysis, the industrial waste of hard chrome collected from industry is situated in Shiroli Industrial Development Maharashtra Corporation (MIDC), near Kolhapur. Industrial effluent was collected, filtered, and diluted with Millipore water till the

TABLE 1 Determination of Cr (VI) ion in synthetic water samples by the standard solution method (n = 3).

		Amount Estimate	of Cr (VI) Ion d		
Source of Water Samples	Synthetic Samples of Cr (VI) added in $\mu g \ mL^{-1}$	By AAS $\mu g \ m L^{-1}$	By proposed method $\mu g m L^{-1} (n = 3)$	% RSD	% recovery
Panchganga River water (Kolhapur, Maharashtra, India)	0.24 0.58	0.240 0.581	0.238 0.579	0.847 0.250	99.311 99.838

TABLE 2 Determination of Cr (VI) ion in real-water samples (waste of hard chrome deposition bath) collected from Maharashtraindustrial estate, Shiroli Kolhapur

	Amount of	Cr (VI) Ion Estimated		
Source of Water Samples	By AAS μg. mL ⁻¹	By proposed method $\mu g m L^{-1} (n = 3)$	% RSD	% Recovery
Near Shivaji University, Shiroli MIDC (Kolhapur, Maharashtra, India).	0.190 0.360	0.190 0.390	0.246 0.786	99.781 100.005

n = number of times experiment repeated.



FIGURE 11 Calibration curve of $(F_0$ -F) versus addition of different amounts of Cr (VI) ion solution (0.0, 0.024, 0.096, 0.14, 0.16, 0.19, 0.24, 0.28, 0.33, 0.38, 0.58 µg mL⁻¹) with error bar

fluorescence intensity of probe with added amount of diluted effluent is within the experimental range of concentration 0.19 and 0.39 (Table 2). The quenching experiment was set procedure used in construction of calibration curve using standard solution of K₂Cr₂O₇ solution. A calibration graph constructed using the fluorescence quenching data of NPs corresponding to $\lambda_{em} = 452$ nm without and with Cr (VI) from S-V plot. The amount of Cr (VI) determined from the calibration graph given in Figure 11 as plot of ΔF (ie, F_0 -F) versus concentration of Cr (VI) with error bar and is straight line passing through origin. The unknown solutions of river, industrial effluent, and hard chrome waste water were analyzed by AAS facility available in our university. The AAS results are given in the same table for the comparison. It is seen that results are concurrent within experimental limit. The amount of Cr (VI) determined from the calibration curve are given in Tables 1 and 2. The result obtained from Tables 1 and 2 recommends that the proposed method has good recovery.

4 | CONCLUSION

Cetyltrimethylammonium bromide (CTAB)-capped highly fluorescent nanoparticles of functionalized 9, 10-DPA attracted selectively $Cr_2O_7^{2-}$ ion from aqueous solution because of surface charge modification created by CTAB. The DLS studies indicated narrower particle size distribution with average size of 72 nm. FE-SEM image showed brick-shaped uniformly distributed particles. The $Cr_2O_7^{2-}$ ion adsorbed on the surface destabilized nanoparticles due to interaction between polar part of CTAB and $Cr_2O_7^{2-}$, and fluorescence of nanoparticle is quenched. The quenching constant estimated from Stern-Volmer equation and adsorption equilibrium constant from Langmuir equation modified for fluorescence quenching data are in close agreement. The present nanoparticle system applied for the determination of Cr (VI) as $Cr_2O_7^{2-}$ from real-water samples is collected from Panchganga River Kolhapur and waste of hard chrome deposition bath collected from Maharashtra Industrial Estate, Shiroli at Kolhapur and analyzed by using method. The recovery data by our method match with the data obtained on Atomic Absorption Spectroscopy method. Thus, the proposed method based on fluorescence "turnoff" of nanoparticles of DPA is simple, selective, and more sensitive because of AIEE from nanoparticles.

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ORCID

Sonali B. Suryawanshi D https://orcid.org/0000-0001-5652-3693

Shivajirao R. Patil D https://orcid.org/0000-0001-8454-589X

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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